

# IONIC EQUILIBRIUM-II

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## 8.1 INTRODUCTION

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In the previous unit you have learnt about the introductory aspects of ionic equilibrium i.e., the equilibria involving ionic species. We began with electrolytes, their types, their ionisation behavior and factors affecting their ionisation behaviour. This was followed by a review of different theories of acids and bases and an important aspect of aqueous solutions viz., autoprotolysis of water. The autoprotolysis of water was then used to define ionic product of water. After discussing its significance we introduced the concept of pH and we also took up calculation of pH for aqueous solutions of strong acids, bases and their mixtures.

In the present unit we would continue our discussion on ionic equilibrium and take up the ionisation of weak acids and bases, the quantitative characterisation of their ionisation equilibria and calculation of pH values of solutions of weak acids and bases. This would be followed by the discussion on ionisation behaviour of diprotic and polyprotic acids, the corresponding ionisation constants and their significance. We would then take up the relationship between the strengths of acids and bases and their molecular structure. Thereafter, the effect of common ions on the ionisation equilibria of

weak acids and bases would be taken up leading to the introduction of concept of buffer solutions. We would explain buffer action and derive an expression to calculate the pH of buffer solutions and calculate the pH values of some common buffer systems. In the end we would discuss about buffer capacity.

In the next unit we would continue our discussion on ionic equilibria and take up the equilibria in aqueous solutions of different types of salts wherein we would talk about hydrolysis of salts and characterisation of the corresponding equilibria. The next unit would also cover the solubility equilibrium of sparingly soluble salts and its applications.

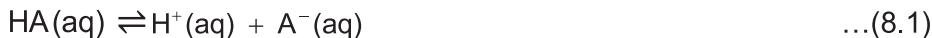
## Expected Learning Outcomes

After studying this unit, you should be able to:

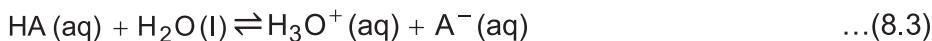
- ❖ explain the ionisation of weak acids and bases and write down the expressions for the corresponding ionisation constants;
- ❖ state the significance of the magnitude of ionisation constants of weak acids and bases;
- ❖ calculate the pH of solutions of weak acids and bases;
- ❖ describe the stepwise ionisation of diprotic and polyprotic acids and write expressions for the respective ionisation constants;
- ❖ calculate the concentration of different species in a solution of a triprotic or polyprotic acid;
- ❖ relate the strengths of acids and bases with their molecular structure;
- ❖ explain the effect of common ions on the ionisation equilibria of weak acids and bases;
- ❖ define buffer solutions and give examples of some common buffer systems;
- ❖ explain buffer action with the help of suitable examples;
- ❖ derive Henderson-Hasselbalch equation for calculating the pH of a buffer solution;
- ❖ calculate the pH values of the solutions of some common buffer systems; and
- ❖ explain the meaning of buffer capacity and state the factors that affect the buffer capacity.

## 8.2 IONISATION CONSTANTS OF WEAK ACIDS AND BASES

You would recall from the previous unit that according to the Arrhenius theory, weak acids and weak bases are the ones which do not ionise completely in aqueous solutions and there exists equilibrium between the ionised and unionised species in the solution. For example, for a weak acid HA, and for a weak base BOH, we can write the ionisation equilibria as



On the other hand, according to the Brønsted and Lowry theory the equilibrium in an aqueous solution of weak acid HA can be given as under:



As stated before, ionisation and dissociation are used interchangeably therefore; acid ionisation is also called acid dissociation. Similarly, acid ionisation constant is also called acid dissociation constant.

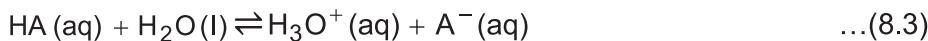
The acid HA reacts with water to produce hydronium ion and the conjugate base, A<sup>-</sup>. The ionisation equilibrium concerning a weak base, B according to the Brønsted and Lowry theory can be given as under:



The process of ionisation of a weak acid (or weak base) in aqueous solution is called **acid (or base) ionisation** and the equilibrium given above is called **acid (or base) ionisation equilibrium**. This equilibrium is characterised by a constant called **ionisation equilibrium constant** or simply **ionisation constant**. Let us derive the expression for the ionisation constant for a weak acid.

### 8.2.1 Ionisation Constant for a Weak Acid

As given above, the ionisation equilibrium for a weak acid, HA can be written as



In order to derive an expression for the ionisation constant characterising this equilibrium, let us take  $c \text{ mol dm}^{-3}$  solution of the weak acid, HA and assume that the degree of ionisation at this concentration is  $\alpha$ . The initial and equilibrium concentrations of different species in the solution would be as:

Concentration /mol dm <sup>-3</sup>	$\text{HA(aq)}$	$\text{H}_2\text{O(l)}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+(\text{aq})$	+	$\text{A}^-(\text{aq})$
Initial	$c$			0		0
Change due to ionisation	$-c\alpha$			$c\alpha$		$c\alpha$
At equilibrium	$c(1-\alpha)$			$c\alpha$		$c\alpha$

The equilibrium constant for the ionisation equilibrium can be written as

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad \dots(8.5)$$

Here, the subscript 'a' in the symbol for equilibrium constant indicates acid. Also note that the concentration of water does not appear in the equilibrium constant expression, as it does not change and is included in  $K_a$ .

Substituting the concentrations of different species at equilibrium in the expression we get,

$$K_a = \frac{c\alpha \times c\alpha}{c(1-\alpha)} \Rightarrow K_a = \frac{c\alpha^2}{(1-\alpha)} \quad \dots(8.6)$$

The value of  $K_a$  is indicative of the strength of the acid, higher the value, stronger the acid. As you can note that the ionisation constant is directly proportional to the square of the degree of ionisation, which means that a higher value refers to higher degree of ionisation. This in turn means that the acid would produce more hydronium ions in solution i.e., the acid is stronger. The ionisation constant values for some common weak acids at 298K are given in Table 8.1

Higher the  $K_a$ , higher the ionisation and hence stronger the acid

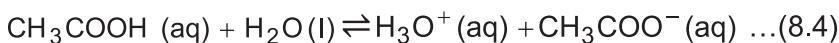
**Table 8.1: Ionisation constants for some weak acids at 298 K**

Name of the weak acid	Molecular formula	Ionisation constant, $K_a$
Chloroacetic acid	$\text{ClCH}_2\text{COOH}$	$1.4 \times 10^{-3}$
Hydrofluoric acid	HF	$7.1 \times 10^{-4}$
Formic acid	$\text{HCOOH}$	$1.7 \times 10^{-4}$
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$	$6.5 \times 10^{-5}$
Acetic acid	$\text{CH}_3\text{COOH}$	$1.8 \times 10^{-5}$
Hydrocyanic acid	HCN	$4.9 \times 10^{-10}$

You would recall from the Ostwald's dilution law discussed in the previous unit that the degree of ionisation depends on the dilution (or concentration) of the electrolyte. As weak acids are weak electrolytes, these would also ionise to different extent as a function of concentration. We can use ionisation constant to determine the degree of ionisation of the weak acid in a solution, which in turn can be used to calculate the pH of a solution of the weak acid. Let us take up an example

**Example 8.1:** Calculate the degree of ionisation and the pH of a 0.1 M aqueous solution of acetic acid at 298K.  
[Given,  $K_a (\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$  at 298K]

**Solution:** The equilibrium reaction for the ionisation of acetic acid, can be given as under:



If the degree of ionisation of acetic acid in this solution is taken as  $\alpha$ , the initial and equilibrium concentrations of various species in the solution would be:

Concentration/ mol dm <sup>-3</sup>	$\text{CH}_3\text{COOH} \text{ (aq)} + \text{H}_2\text{O} \text{ (l)} \rightleftharpoons \text{H}_3\text{O}^+ \text{ (aq)} + \text{CH}_3\text{COO}^- \text{ (aq)}$		
Initial	0.1	0	0
Change due to ionisation	$-0.1\alpha$	$0.1\alpha$	$0.1\alpha$
At equilibrium	$0.1(1-\alpha)$	$0.1\alpha$	$0.1\alpha$

We can write the expression for  $K_a$  as:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Substituting the equilibrium concentrations of different species from the table, we get

$$\Rightarrow K_a = \frac{(0.1\alpha)(0.1\alpha)}{0.1(1-\alpha)} = \frac{0.1\alpha^2}{(1-\alpha)}$$

Assuming that  $\alpha$  is small as compared to 1, we can ignore it in the denominator; we get,  $K_a = 0.1\alpha^2$

On rearranging it gives,

$$\alpha = \sqrt{\frac{K_a}{0.1}}$$

Substituting the values of  $K_a$ ,

$$\alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.1}} = \sqrt{1.8 \times 10^{-4}} = 0.0134$$

→ Degree of ionisation of acetic acid in 0.1 M solution = 0.0134

Percentage ionisation = Degree of ionisation  $\times 100 = 0.0134 \times 100 = 1.34\%$

This means that at a concentration of 0.1 M, 1.34 % of the molecules of acetic acid are ionised; it translates to 134 molecules per 10000 molecules. Let us now calculate the value of pH for the solution

From the table above, we see that the concentration of hydronium ions,  $[\text{H}_3\text{O}^+]$  at equilibrium  $= 0.1 \times \alpha = 0.1 \times 0.0134 = 1.34 \times 10^{-3}$  M. This can be used to calculate the pH as follows:

$$\rightarrow \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log [1.34 \times 10^{-3}]$$

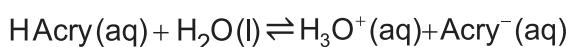
$$\text{pH} = -(-2.87) = 2.87$$

Thus, the pH of the 0.1 M aqueous solution of acetic acid would be 2.87

Having learnt to compute the pH of a given solution of weak acid using its  $K_a$  value, let us take another example to calculate the  $K_a$  value of a weak acid using the pH of its given solution.

**Example 8.2:** A 0.10 M aqueous solution of acrylic acid-a weak acid used in manufacture of plastics has a pH of 2.63. Calculate the value of  $K_a$  for acrylic acid?

**Solution:** The ionisation equilibrium of acrylic acid can be given as under:



If the degree of ionisation of acrylic acid in this solution is taken as  $\alpha$ , the initial and equilibrium concentrations of various species would be

Concentration/ mol dm <sup>-3</sup>	HAcry (aq) + H <sub>2</sub> O (l) ⇌ H <sub>3</sub> O <sup>+</sup> (aq) + Acry <sup>-</sup> (aq)		
Initial	0.10	0	0
Change due to ionisation	- 0.10 $\alpha$	0.10 $\alpha$	0.10 $\alpha$
At equilibrium	0.10 (1 - $\alpha$ )	0.10 $\alpha$	0.10 $\alpha$

As per the table given above, the concentration of hydronium ion at equilibrium would be  $0.10\alpha$ . We are given the pH of the solution as 2.63, which can be used to calculate the concentration of hydronium ions. Equating the two we can get the value of  $\alpha$  which can then be used to calculate the value of  $K_a$ . Let's proceed by computing the concentration of hydronium ions first

We know that  $pH = -\log_{10} [H_3O^+] \rightarrow [H_3O^+] = \text{antilog}(-pH)$

$$\Rightarrow [H_3O^+] = \text{antilog}(-2.63) = 2.34 \times 10^{-3} \text{ M}$$

Equating the expression for equilibrium concentration of hydronium ions with this calculated value:

$$\Rightarrow 0.10 \alpha = 2.34 \times 10^{-3}$$

$$\text{we get } \alpha = 2.34 \times 10^{-2}$$

We know that the  $K_a$  for a weak acid whose  $c$  molar solution has degree of ionisation  $\alpha$ , is given by the following expression.

$$\Rightarrow K_a = \frac{c\alpha^2}{(1-\alpha)} \quad \dots(8.6)$$

Substituting the values of  $c$  and  $\alpha$

$$\Rightarrow K_a = \frac{0.1 \times (2.34 \times 10^{-2})^2}{(1 - 0.0234)}$$

$$\Rightarrow K_a = \frac{0.1 \times 5.48 \times 10^{-4}}{0.9766}$$

$$\Rightarrow K_a = \frac{0.1 \times 5.48 \times 10^{-4}}{0.9766} = 5.61 \times 10^{-5}$$

The  $K_a$  value for the acrylic acid is found to be  $= 5.61 \times 10^{-5}$

## 8.2.2 Ionisation Constant for a Weak Base

Let's now take up the ionisation equilibrium for a weak base, B and derive an expression for its ionisation constant. As per Brønsted and Lowry theory, the ionisation of the weak base, B in aqueous solution can be written as



If we start with  $c$  mol dm<sup>-3</sup> of the weak base and assume that the degree of ionisation at this concentration is  $\alpha$ , the initial and equilibrium concentrations of different species in the solution would be as follows

Concentration / mol dm <sup>-3</sup>	$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$		
Initial	$c$	0	0
Change due to ionisation	$-c\alpha$	$c\alpha$	$c\alpha$
At equilibrium	$c(1-\alpha)$	$c\alpha$	$c\alpha$

The equilibrium constant for the ionisation equilibrium for the weak base, B can be written as

$$K_b = \frac{[BH^+] [OH^-]}{[B]} \quad \dots(8.8)$$

Here, the subscript b in the symbol for equilibrium constant indicates base. Also note that the concentration of water does not appear in the equilibrium expression as its concentration remains constant and is included in  $K_b$ .

Substituting the concentrations of different species from the table in the base ionisation constant expression we get,

$$K_b = \frac{c\alpha \times c\alpha}{c(1-\alpha)} \quad K_b = \frac{c\alpha^2}{(1-\alpha)} \quad \dots(8.9)$$

The value of  $K_b$  is indicative of the strength of the base. As ionisation constant is directly proportional to the square of the degree of ionisation, a higher value of ionisation constant refers to higher degree of ionisation or a stronger base. The ionisation constant values of some common weak bases at 298K are given in Table 8.2.

Table 8.2: Ionisation constants for some weak bases at 298 K

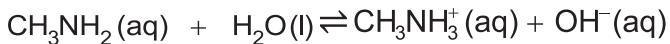
Name of the weak base	Molecular formula	Ionisation constant, $K_b$
Diethylamine	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NH	$6.9 \times 10^{-4}$
Dimethylamine	(CH <sub>3</sub> ) <sub>2</sub> NH	$5.1 \times 10^{-4}$
Ethylamine	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	$4.3 \times 10^{-4}$
Methylamine	CH <sub>3</sub> NH <sub>2</sub>	$4.4 \times 10^{-4}$
Ammonia	NH <sub>3</sub>	$1.8 \times 10^{-5}$
Hydroxylamine	NH <sub>2</sub> OH	$1.1 \times 10^{-8}$
Aniline	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	$4.2 \times 10^{-10}$

As in the case of weak acids discussed above, we can use ionisation constant of a weak base to determine the degree of ionisation of the weak base, which

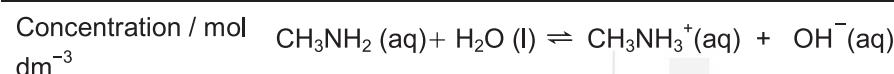
in turn can be used to calculate the pH of a solution of a weak base. Let us take up an example

**Example 8.3:** Calculate the degree of ionisation and the pH of a 0.1 M solution of methylamine,  $\text{CH}_3\text{NH}_2$  at 298 K.  
[Given,  $K_b (\text{CH}_3\text{NH}_2) = 4.4 \times 10^{-4}$ ]

**Solution:** The ionisation equilibrium of methylamine in water, can be given as under:



If the degree of ionisation of methylamine in the 0.1 M solution is taken as  $\alpha$ , the initial and equilibrium concentrations of various species in the solution would be



Initial	0.1	0	0
Change due to ionisation	$-0.1\alpha$	$0.1\alpha$	$0.1\alpha$
At equilibrium	$0.1(1-\alpha)$	$0.1\alpha$	$0.1\alpha$

We can recall the expression for  $K_b$ , Eq. (8.9)

$$K_b = \frac{c\alpha^2}{(1-\alpha)}$$

Assuming that  $\alpha$  is small as compared to 1, we can ignore it in the denominator of Eq. (8.9), we get  $K_b = c\alpha^2$

$$\text{Which gives } \alpha = \sqrt{\frac{K_b}{c}}$$

Substituting the values of  $K_b$  and  $c$  we get,

$$\alpha = \sqrt{\frac{4.4 \times 10^{-4}}{0.1}} = \sqrt{4.4 \times 10^{-3}} = 0.066$$

Degree of ionisation of methylamine in 0.1 M aqueous solution = 0.066

Percentage ionisation = degree of ionisation  $\times 100 = 0.066 \times 100 = 6.6\%$

This means that at a concentration of 0.1 M, 6.6 % of the molecules of methylamine are ionised. As the value of degree of ionisation (0.066) is more than 5% of the initial concentration, our assumption of it being small and neglecting it is not valid. So we cannot ignore it. We go back to Eq. (8.9), we had

$$\Rightarrow K_b = \frac{c\alpha^2}{(1-\alpha)} \quad \dots(8.9)$$

Substituting the values of  $K_b$  and  $c$ , we get

$$\Rightarrow 4.4 \times 10^{-4} = \frac{0.1\alpha^2}{(1-\alpha)}$$

On simplification,

$$\Rightarrow (4.4 \times 10^{-4}) - (4.4 \times 10^{-4})\alpha = 0.1\alpha^2$$

On rearranging,

$$\Rightarrow 0.1\alpha^2 + (4.4 \times 10^{-4})\alpha - (4.4 \times 10^{-4}) = 0$$

We need to solve the above quadratic equation to get the value of the degree of ionisation,  $\alpha$ . As you know that for a quadratic equation,  $ax^2 + bx + c = 0$ , the value of  $x$  can be obtained by the following expression

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In the present case we can write

$$\alpha = \frac{-(4.4 \times 10^{-4}) \pm \sqrt{(4.4 \times 10^{-4})^2 - 4 \times 0.1 \times (4.4 \times 10^{-4})}}{2 \times 0.1}$$

Solving we get,

$$\alpha = \frac{-(4.4 \times 10^{-4}) \pm \sqrt{(1.936 \times 10^{-7}) + (1.76 \times 10^{-4})}}{0.2}$$

$$\alpha = \frac{-(4.4 \times 10^{-4}) \pm \sqrt{1.76 \times 10^{-4}}}{0.2}$$

$$\alpha = \frac{-(4.4 \times 10^{-4}) \pm 1.327 \times 10^{-2}}{0.2} = \frac{1.28 \times 10^{-2}}{0.2} = 6.4 \times 10^{-2}$$

$$\alpha = 6.4 \times 10^{-2} \quad (\text{ignoring the negative root})$$

From the table above, we see that the concentration of hydroxide ions,  $[\text{OH}^-]$  at equilibrium =  $0.1 \times \alpha = 0.1 \times 0.064 = 0.0064 = 6.4 \times 10^{-3} \text{ M}$

$$\text{pOH} = -\log[\text{OH}^-] = -\log[6.4 \times 10^{-3}]$$

$$\text{pOH} = -(2.19) = 2.19$$

we know that at 298 K,

$$\text{pH} = 14 - \text{pOH}$$

$$\Rightarrow \text{pH} = 14 - 2.19 = 11.81$$

Having learnt about the ionisation of weak acids and bases and characterisation of their equilibria in terms of the respective ionisation constants it is time we take up the ionisation behaviour of diprotic and polyprotic acids. These acids can generate or donate two or more protons in

solution. However, before moving ahead answer the following self-assessment questions to gauge your understanding of ionisation of weak acids and bases.

### SAQ 1

Give the expression relating the ionisation constant of a weak acid with its degree of ionisation and discuss the significance of the magnitude of ionisation constant.

### SAQ 2

Morphine is an alkaloid found naturally in a number of plants and animals and is used as a medicine to relieve pain. It is a weak base having  $K_b = 1.6 \times 10^{-6}$ . Calculate the pH of 0.01 M aqueous solution of morphine at 298 K.

## 8.3 IONISATION OF DIPROTIC AND POLYPYRATIC ACIDS

The weak acids discussed above had only one ionisable hydrogen atom i.e., they generate only one hydrogen ion in aqueous solution even if they may have more than one hydrogen atom. On the other hand, a number of acids have two or more than two ionisable hydrogen atoms. Accordingly, these are called diprotic or polyprotic acids. The acids containing three ionisable hydrogen atoms are sometimes called triprotic acids. These acids ionise in a stepwise manner; i.e., they sequentially lose one hydrogen ion at a time. To begin with let us learn about the ionisation of a diprotic acid.

### 8.3.1 Ionisation of Diprotic Acids

In order to understand the ionisation behaviour of diprotic acids we take the example of carbonic acid,  $\text{H}_2\text{CO}_3$ . The successive ionisation equilibria for  $\text{H}_2\text{CO}_3$  can be given as



Where,  $K_{a1}$  and  $K_{a2}$  are the ionisation constants of the first and the second stage of ionisation respectively. The expressions for the ionisation constants and their experimental values at 298 K are

$$K_{a1} = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{CO}_3]} = 4.3 \times 10^{-7} \quad \dots(8.12)$$

$$K_{a2} = \frac{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]} = 4.8 \times 10^{-11} \quad \dots(8.13)$$

You may note here that the first ionisation constant,  $K_{a1}$  is about 10,000 times larger than the second ionisation constant,  $K_{a2}$ . In general, the successive

ionisation constants for di and polyprotic acids get smaller and smaller. Can you think of a reason for the same? The reason is quite simple, in case of first ionisation the proton is getting lost from a neutral species or we may say that it is removed from a species with one unit of negative charge. On the other hand, in case of second ionisation, we need to remove a proton from a species with two units of negative charge which is relatively difficult. In general in successive ionisations a proton is removed from more and more negatively charged species.

### **8.3.2 Ionisation of Triprotic Acids**

As the name suggests, triprotic acids have three ionisable protons that ionise successively. The ionisation equilibria corresponding to the successive ionisation of a triprotic acid, for example,  $\text{H}_3\text{PO}_4$  can be given as



Where,  $K_{a1}$ ,  $K_{a2}$  and  $K_{a3}$  are the ionisation constants of the first, second and the third stage of ionisation respectively. The expressions for the ionisation constants and their experimental values at 298 K are

$$K_{a1} = \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_4]}; \quad = 7.1 \times 10^{-3} \quad \dots(8.17)$$

$$K_{a2} = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]} \quad = 6.3 \times 10^{-8} \quad \dots(8.18)$$

$$K_{a3} = \frac{[\text{PO}_4^{3-}][\text{H}_3\text{O}^+]}{[\text{HPO}_4^{2-}]} \quad = 4.2 \times 10^{-13} \quad \dots(8.19)$$

Here again you may note that the successive ionisation constants get smaller and smaller. In order to get an insight into the equilibria involved in di- and polyprotic acids it is worthwhile to calculate the concentration of various species in an aqueous solution of such acids. We take the example of 1.0 M solution of phosphoric acid.

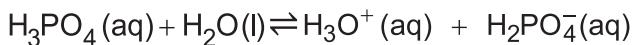
**Example 8.4:** Calculate the concentrations of the following species in a 1.0 M aqueous solution of phosphoric acid



The values of successive equilibrium constants are given as

$$K_{a1} = 7.1 \times 10^{-3}; \quad K_{a2} = 6.3 \times 10^{-8}; \quad \text{and} \quad K_{a3} = 4.2 \times 10^{-13}$$

**Solution:** To begin with we assume that in the first stage of ionisation phosphoric acid behaves as a weak acid and the corresponding equilibrium reaction can be given as;



The initial and equilibrium concentrations of different species in the solution would be as follows

Concentration mol dm <sup>-3</sup>	$\text{H}_3\text{PO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{H}_2\text{PO}_4^-(\text{aq})$		
Initial	1.0	0	0
Change due to ionisation	$-\alpha$	$\alpha$	$\alpha$
At equilibrium	$1 - \alpha$	$\alpha$	$\alpha$

The equilibrium constant for the ionisation reaction is given as

$$K_{a1} = \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_4]} \quad \dots (8.17)$$

We recall the relationship between  $K_a$  and  $\alpha$  for a weak acid; Eq. (8.6)

$$K_a = \frac{c\alpha^2}{(1-\alpha)} \quad \dots (8.6)$$

Substituting the value of  $K_a$  and  $c$  in the ionisation constant expression, we get,

$$7.1 \times 10^{-3} = \frac{(\alpha^2)}{(1-\alpha)}$$

If we assume the first ionisation of phosphoric acid to be like a weak acid, and ignore  $\alpha$  in the denominator of the above expression, we get

$$\alpha^2 = 7.1 \times 10^{-3} \Rightarrow \alpha = 0.0843$$

The value of  $\alpha$  comes to be 0.0843 (i.e., 8.43%), which is more than 5% of the initial concentration. Thus, our assumption is not valid and we cannot ignore  $\alpha$ . Going back to Eq. (8.6)

$$7.1 \times 10^{-3} = \frac{(\alpha^2)}{(1-\alpha)}$$

Simplifying and rearranging, we get

$$\alpha^2 + (7.1 \times 10^{-3})\alpha - (7.1 \times 10^{-3}) = 0$$

So we need to solve the following quadratic equation to get the value of  $\alpha$ .

$$\alpha^2 + 0.0071\alpha - 0.0071 = 0$$

Recall that for a quadratic equation  $ax^2 + bx + c = 0$ , the value of the root,  $x$  can be obtained by the following equation.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

So for our equation,

$$\Rightarrow \alpha = \frac{-(0.0071) \pm \sqrt{(0.0071)^2 - 4 \times 1 \times (-0.0071)}}{2}$$

$$\Rightarrow \alpha = \frac{-(0.0071) \pm \sqrt{(0.0000504) + (0.0284)}}{2}$$

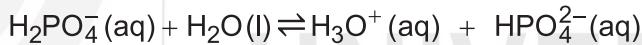
$$\Rightarrow \alpha = \frac{-(0.0071) \pm \sqrt{0.0284504}}{2}$$

$$\Rightarrow \alpha = \frac{-(0.0071) \pm 0.1687}{2} = \frac{0.1616}{2} = 0.0808$$

Thus, solving the equation gives the value of  $\alpha$  as 0.0808. This in fact gives the concentrations of  $[H_2PO_4^-]$ , as well as that of  $[H_3O^+]$ . (See the equilibrium concentrations in the above table)

$$\Rightarrow [H_3O^+] = [H_2PO_4^-] = \alpha = 0.0808 = 8.08 \times 10^{-2} M$$

The consideration of second stage of ionisation would help us get the concentration of  $[HPO_4^{2-}]$ . The ionisation equilibrium for the second stage of the ionisation would be



The initial and equilibrium concentrations of different species in the solution would be as follows

Concentration/mol dm <sup>-3</sup>	$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$		
Initial	0.0808	0.0808	0
Change due to ionisation	$-\alpha$	$+\alpha$	$+\alpha$
At equilibrium	$0.0808 - \alpha$	$0.0808 + \alpha$	$\alpha$

The equilibrium constant for the ionisation reaction is given as

$$K_{a2} = \frac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]} \quad \dots(8.18)$$

Substituting the equilibrium concentrations from the table in the equilibrium constant expression, we get

$$\frac{[0.0808 + \alpha][\alpha]}{[0.0808 - \alpha]} = 6.3 \times 10^{-8}$$

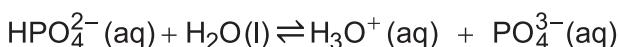
Assuming  $\alpha$  to be negligible as compared to the initial concentration (0.0808 M) we get

$$\frac{[0.0808][\alpha]}{[0.0808]} = 6.3 \times 10^{-8} \Rightarrow \alpha = 6.3 \times 10^{-8}$$

So the concentration of  $\text{HPO}_4^{2-}$  ions would be  $= 6.3 \times 10^{-8}$  M which is equal to the second ionisation constant.

You may note here that the concentration ( $6.3 \times 10^{-8}$  M) of hydronium ions produced in this stage of ionisation is much less than that produced in the first stage (0.0808 M). This means that practically all the hydronium ions present in the solution are obtained from the first stage of ionisation. This is a general feature of ionisation of most of the di- and polyprotic acids.

We would now consider the third stage of ionisation of phosphoric acid.



The initial and equilibrium concentrations of different species in the solution would be as follows

Concentration/mol dm <sup>-3</sup>	$\text{HPO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq})$		
Initial	$6.3 \times 10^{-8}$	0.0808	0
Change due to ionisation	$-\alpha$	$+\alpha$	$+\alpha$
At equilibrium	$6.3 \times 10^{-8} - \alpha$	$0.0808 + \alpha$	$\alpha$

The equilibrium constant for the ionisation reaction is given as

$$K_{a3} = \frac{[\text{PO}_4^{3-}][\text{H}_3\text{O}^+]}{[\text{HPO}_4^{2-}]} \quad \dots(8.19)$$

Substituting the equilibrium concentrations from the table in the equilibrium constant expression, we get

$$\frac{[\alpha][0.0808 + \alpha]}{[6.3 \times 10^{-8} - \alpha]} = 4.2 \times 10^{-13}$$

Assuming the value of  $\alpha$  to be negligible as compared to  $6.3 \times 10^{-8}$  (and obviously to 0.0808 M), we get

$$\frac{[\alpha][0.0808]}{[6.3 \times 10^{-8}]} = 4.2 \times 10^{-13}$$

Solving, we get

$$\Rightarrow \alpha = \frac{4.2 \times 10^{-13} \times 6.3 \times 10^{-8}}{0.0808} = 3.27 \times 10^{-19}$$

Therefore, the concentration of phosphate ions in the solution would be  $3.27 \times 10^{-19}$  M. Thus, the concentrations of different ions in the 1.0 M solution of phosphoric acid would be

$$[\text{H}_2\text{PO}_4^-] = 8.08 \times 10^{-2} \text{ M} \quad [\text{HPO}_4^{2-}] = 6.3 \times 10^{-8} \text{ M}$$

$$[\text{PO}_4^{3-}] = 3.27 \times 10^{-19} \text{ M} \quad [\text{H}_3\text{O}^+] = 8.08 \times 10^{-2} \text{ M}$$

From the example given above, you can take note of a few important aspects of ionisation of polyprotic acids

- i) A large amount of the polyprotic acid remains unionized, (in this example;  $1.0 - 0.0808 = 0.9192 \text{ M}$  i.e., about 92%).
- ii) The concentrations of mono-negative ion of the polyprotic acid and the hydronium ions can be obtained by considering just the first stage of ionisation only. These are the only ions whose concentrations are significant and further ionisations do not alter these concentrations significantly.
- iii) The concentration of di-negative ion of the polyprotic acid equals the ionisation constant of second stage

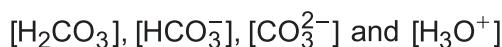
Assess your understanding of ionisation of di- and polyprotic acids by answering the following questions.

### *SAQ 3*

Write down the equilibrium reactions for the successive ionisation of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ )-a diprotic acid. Also give the expressions for the ionisation constants for the reactions.

### *SAQ 4*

Calculate the concentrations of the following species in a 1.0 M aqueous solution of carbonic acid,  $\text{H}_2\text{CO}_3$ . [Given  $K_{a1} = 4.4 \times 10^{-7}$  and  $K_{a2} = 4.7 \times 10^{-11}$ ]



## 8.4 STRENGTHS OF ACIDS AND BASES

We have discussed a number of theories of acids and bases and have talked about strong and weak acids and bases. Have you ever thought what makes an acid (say HCl) strong and a closely related molecule (HF) a weak acid? The strength of an acid or a base depends on a number of factors, like the temperature, nature of solvent, and the molecular structure. In order to understand or determine the relative strengths of acids and bases as a function of their molecular structure, we keep the temperature and the nature of solvent the same and rationalise the relative strength in terms of the molecular structure. Let's make an attempt to understand the relative strengths of acids as a function of their molecular structure. We would take different classes of molecules.

## Strengths of Hydrohalic Acids

You have learnt that one of the requirements for a molecule to behave, as an acid is that it is able to lose or donate a proton. The ease of the process determines its strength as an acid, easier the process stronger the acid. This in turn depends on the strength of the bond between acidic proton and other atoms of the molecule. Let's take a simple case of binary hydrohalic acids of HX type that ionise as



Bond	Bond enthalpy
H-F	568.2
H-Cl	431.9
H-Br	366.1
H-I	298.3

There are two factors that determine the extent of this reaction. The first being the strength of the H-X bond and the second the polarity of the bond. You would recall from your earlier understanding of periodic properties of elements, that when we go down a group of elements in the periodic table, the size of atom X increases, and the strength of H-X bond decreases. This, in turn means that it becomes easier to break the bond and make H<sup>+</sup> available and hence from bond strength considerations the strength of the acid increases down the group. Now let's take up the second factor, i.e., the polarity of the bond. As you know that the polarity of a bond depends on the difference in the electronegativities of the bonded atoms. The electronegativities of the elements decrease down the group. The electronegativity of hydrogen is 2.1, so the difference in electronegativities of the bonded atoms in halogen acids decreases down the group. As the polarity decreases, so is the tendency to lose a proton. In other words, from polarity considerations, the acidity should decrease down the group. Thus, there are two opposing factors: one (bond strength) increasing the strength of acid and the second (polarity) decreasing the strength of the acid as we move down the group. However, it has been experimentally found that the order of acidity of different hydrohalic acids varies as

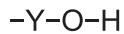


This means that HI is a strong acid whereas HF is a weak acid. This trend indicates that bond enthalpy is more significant factor than bond polarity in determining the acid strength of binary hydrohalic acids

Element	Electro-negativity
Fluorine	4
Chlorine	3
Bromine	2.8
Iodine	2.5

## Strengths of Oxoacids

You would recall from your earlier studies that an oxoacid contains a hydrogen atom attached to an oxygen atom, which, in turn, is attached to another atom Y. The structure of an oxoacid can be represented as



Where, the atom Y is bonded to other atom(s) in the molecule. Since in all oxoacids the acidic H atom is bonded to an oxygen atom, the bond strength is not a distinguishing factor in determining their relative acidity. It is the charge (electrons) on the oxygen atom or the polarity of the O-H bond that is important. This means that the presence of any group that can withdraw electrons from oxygen atom would make the removal of hydrogen ion easier.

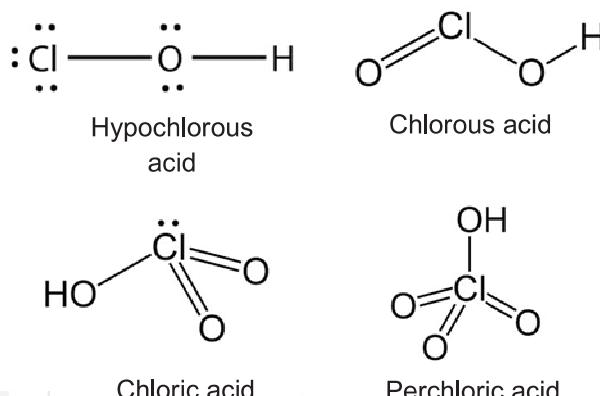
Let's take the example of two simple oxoacids viz., HOCl and HOBr. As the chlorine atom is more electronegative than bromine, it would make oxygen atom relatively more positive in HOCl than that in HOBr. The electronegativity of

Oxoacids and oxyacids are synonymous and are used interchangeably

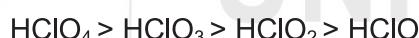
Element	Electro-negativity
Hydrogen	2.1
Oxygen	3.5
Chlorine	3.0
Bromine	2.8

oxygen is 3.5 whereas that for chlorine and bromine is 3.0 and 2.8 respectively. Due to the difference in the electronegativities of oxygen and chlorine/bromine oxygen pulls electrons from both of them but to a lesser extent from chlorine than from bromine. This would make the O–H bond more polar, which means it will be easier for the hydrogen ion to be removed in case of HOCl. That is, it will be the stronger of the two acids. This is substantiated by the experimental data also as the acid dissociation constants for HOCl and HOBr are  $2.9 \times 10^{-8}$  and  $2.3 \times 10^{-9}$  respectively i.e., HOCl is about 12 times stronger than HOBr.

In some of the oxoacids, the atom Y is attached to a number of oxygen atoms. In such cases the number of such oxygen atoms determines the strength of the oxoacid. Higher the number of oxygen atoms stronger is the acid. Let's understand it by taking the example of oxoacids of chlorine. The structures of oxoacids of chlorine are as under



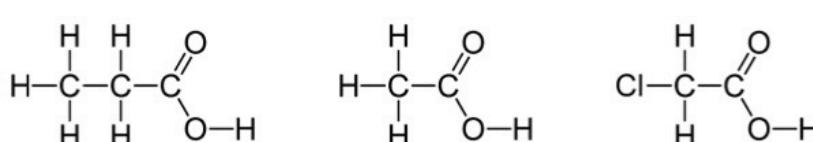
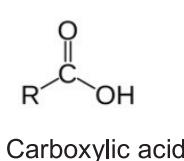
As the number of oxygen atoms attached to the chlorine atom increases, these pull electrons away from the chlorine atom and make it more and more positive. This in turn makes the removal of hydrogen ion easier by decreasing the electron density at the oxygen atom. Experimentally also the acidic strength of these oxoacids is found to vary as



We have so far discussed about the relative strength of inorganic acids. Let's learn about the factors determining the strengths of carboxylic acids.

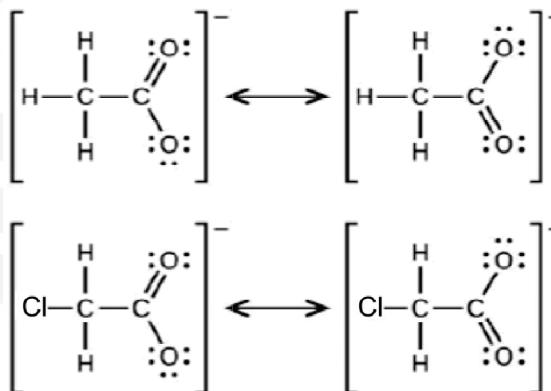
### Strengths of Carboxylic Acids

You know that carboxylic acids are organic acids containing –COOH functional group. Different carboxylic acids differ in terms of the structure and nature of R group. Let us take three closely related carboxylic acids viz., ethanoic acid (acetic acid), 2-chloroethanoic acid and propanoic acid whose structures are given below



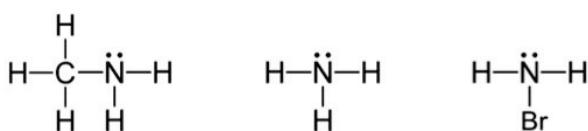
In this example we take ethanoic acid as representative carboxylic acid and the other two molecules as its derivatives so as to understand the effect of structure of R group. Ethanoic acid is a weak acid characterised by its acid dissociation constant of  $1.8 \times 10^{-5}$ . In case of 2-chloroethanoic acid highly electronegative chlorine atom withdraws electrons from carbon atom to which it is attached. This in turn pulls electrons from the carbon atom of the carboxylic group thereby making the O-H bond more polar and the strength of the acid increases,  $K_a=1.4 \times 10^{-3}$ . 2-chloroethanoic acid is about seventy seven times stronger than ethanoic acid. On the other hand, propanoic acid may be considered as a derivative of ethanoic acid in which a methyl group replaces one of the hydrogen atoms of the methyl group attached to carbon atom of carboxylic acid group. As you are aware, the methyl group is electron-donating group, it would increase the electron density at the carbon atom to which it is attached. This in turn donates electrons to the carbon atom of the carboxylic group thereby making the O-H bond lesser polar and the strength of the acid decreases,  $K_a= 1.4 \times 10^{-5}$ . As the electron donating effect of methyl group is much weaker than the electron withdrawing effect of chlorine atom, propanoic is only slightly weaker than ethanoic acid.

In addition to the electron withdrawing or electron donating effects of the substituents, the stability of the anion formed as a consequence of ionisation of the acid is also an important factor. 2-chloroethanoate ion obtained from the ionisation of 2-chloroethanoic acid is more resonance stabilised than the ethanoate ion obtained from the ionisation of ethanoic acid. The chlorine atom pulls the electrons from the carboxylate ion and stabilises the structure.



### Strengths of Simple Bases

Having learnt about the relative acidities of different types of acids let's take up the basicity of simple amines. You know that ammonia is basic as it can donate its lone pair (present on nitrogen atom). Once again we take three closely related molecules, viz., ammonia, bromamine and methylamine whose structure are given below to understand the relationship between molecular structure and basicity.



methylamine

ammonia

bromamine

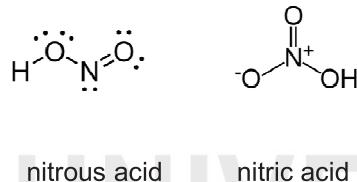
In ammonia, there is a lone pair of electrons available on the nitrogen atom. In addition the N atom pulls electrons from the three hydrogen atoms due to the difference in electronegativities. This accumulates negative charge on the nitrogen atom and N atom can easily donate its lone pair of electrons, thus making ammonia basic ( $K_b=1.82 \times 10^{-5}$ ). In case of bromamine, one of the hydrogen atoms of ammonia is replaced by a bromine atom. As the electronegativity of Br (2.8) is higher than that of H (2.1), the nitrogen atom is not able to pull electrons from it as effectively as was with H atom. As a consequence, the negative charge accumulation on nitrogen atom decreases. This leads to a relatively lower ease of donating lone pair of electrons by nitrogen and hence the basicity decreases. In other words, bromamine is a weaker base than ammonia. On the other hand, in case of methylamine, the methyl group being electron-donating group increases the availability of lone pair on the nitrogen atom. This makes methylamine a stronger base than ammonia. Thus, the order of basicity of these molecules should be



The experimental values of base dissociation constants,  $K_b$ 's for methylamine, ammonia and bromamine being  $4.17 \times 10^{-4}$ ,  $1.82 \times 10^{-5}$  and  $2.45 \times 10^{-8}$  respectively support the above given order of basicity.

### SAQ 5

The structures of nitrous and nitric acids are given as under.



Which of these acids would be stronger and why?

## 8.5 COMMON ION EFFECT

In Unit 6 you have learnt about Le-Chatelier principle that deals with the effect of different factors on the systems under equilibrium. As weak acids and bases also exhibit systems in equilibrium we expect these equilibria also to be affected by such factors. Here we would consider the effect of adding a solute, having an ion common with the weak acid or base, to an aqueous solution of weak acid or base as the case may be. To begin with, let's consider a weak acid HA that ionises as



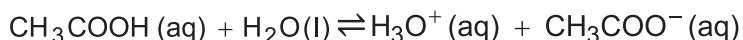
What will happen if to an aqueous solution of acid HA we add a solution of a salt NaA? NaA being a strong electrolyte will dissociate completely into the ions as follows



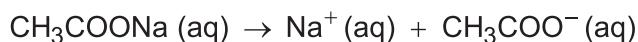
The  $A^-$  ions provided by the salt appear on the product side of the above equilibrium, Eq.(8.1) so according to Le-Chatelier principle they will make the equilibrium shift to the left. We say that the common ions have suppressed the ionisation of the weak acid or in other words, the degree of ionisation of weak acid would decrease. Let us take an example to understand the effect of common ions on the ionisation equilibrium of a weak acid

**Example 8.5:** An aqueous solution contains 0.1 M each of acetic acid and sodium acetate. Calculate the degree of ionisation of acetic acid and the pH of the solution. Compare your results with the ones obtained in example 8.1.

**Solution:** The equilibrium for the ionisation of acetic acid, can be given as under:



The salt sodium acetate would dissociate as



If the degree of ionisation of acetic acid in this solution is taken as  $\alpha$ , the initial and equilibrium concentrations of various species in the solution would be

Concentration / mol dm <sup>-3</sup>	$\text{CH}_3\text{COOH} \text{ (aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+ \text{ (aq)} + \text{CH}_3\text{COO}^- \text{ (aq)}$			
Initial	0.1	0	0	
Change due to ionisation of acetic acid	$-0.1\alpha$	$0.1\alpha$	$0.1\alpha$	
Change due to dissociation of sodium acetate	0	0	0.1	
At equilibrium	$0.1(1-\alpha)$	$0.1\alpha$	$0.1(1+\alpha)$	

We can write the expression for acid ionisation constant of acetic acid as

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Substituting the equilibrium concentrations of different species from the table above, in the equilibrium constant expression, we get

$$K_a = \frac{[0.1\alpha][0.1(1+\alpha)]}{[0.1(1-\alpha)]}$$

As acetic acid is a weak acid and its degree of ionisation which is already low is further suppressed by the presence of acetate ions (the common ion) we can reasonably assume that

$$\alpha \ll 1; \text{ and } (1-\alpha) \sim 1; \text{ also } (1+\alpha) \sim 1$$

The shift in equilibrium of a weak acid / base caused by the addition of a salt having an ion in common with the weak acid /base is called **common ion effect**.

Under these conditions we write

$$K_a = \frac{[0.1\alpha][0.1]}{[0.1]} = [0.1\alpha]$$

Substituting the value of the acid ionisation constant,  $K_a$

$$1.8 \times 10^{-5} = [0.1\alpha] \Rightarrow \alpha = 1.8 \times 10^{-4}$$

So the degree of ionisation of acetic acid in the given solution = 0.00018.

Percentage ionisation = degree of ionisation  $\times 100 = 0.00018 \times 100 = 0.018\%$

Recall that in example 8.1 we computed the degree of ionisation of 0.1 M acetic acid (without any salt) to be = 0.0134 or 1.34%. Thus, the addition of 0.1 M sodium acetate has drastically reduced the degree of ionisation of acetic acid [from 1.34 % to 0.018 %]. You can note here that the presence of common ions have decreased the extent of ionisation by as much as 74 times.

Let's now calculate the pH. As per the table, the concentration of hydronium ions at equilibrium =  $0.1\alpha$

$$\rightarrow [\text{H}_3\text{O}^+]_{\text{equilibrium}} = 0.1 \times \alpha = 0.1 \times 0.00018 = 1.8 \times 10^{-5}$$

we know that

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

Substituting the value of  $[\text{H}_3\text{O}^+]$ ,

$$\text{pH} = -\log [1.8 \times 10^{-5}]$$

$$\text{pH} = -( -4.74 ) = 4.74$$

Once again recalling from example 8.1, the pH of 0.1 M acetic acid (without any salt) was computed to be 2.87; the addition of 0.1 M sodium acetate has **increased the pH from 2.87 to 4.75.**

Similarly, we can deal with the aqueous solutions of weak bases containing a salt having a common ion. In such cases also the degree of ionisation would decrease. What do you think would be the effect on pH of the solution of a weak base? Will it increase or decrease? Write your response here before proceeding further.

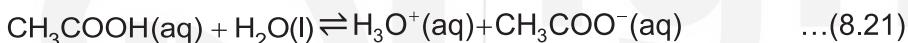
The decrease in the degree of ionisation of a weak base means that the concentration of hydroxyl ions would decrease which implies that the concentration of hydronium ions would increase. Therefore the pH of an aqueous solution of weak base would **decrease** on adding a salt having a common ion. Let us take up an important type of solutions that exploit the change in pH of a weak acid or a base on adding a salt containing common ions.

## 8.6 BUFFER SOLUTIONS

If we repeat the calculations given in example 8.5 for a solution containing 0.1 M acetic acid and 0.2 M sodium acetate we find that the degree of ionisation further decreases to 0.00009 and the pH increases to 5.04. This indicates that the pH of aqueous solutions of weak acids or bases can be controlled by adding suitable amounts of a salt containing common ion. The aqueous solutions containing weak acids or weak bases and a salt of common ion are quite important as these act as buffer solutions. A *buffer solution* is defined as a solution that resists the change in its pH on adding small volumes of strong acid / base or on dilution. The buffer solutions containing weak acid and its salt are called **acidic buffer solutions** e.g. acetic acid and sodium acetate,  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ . On the other hand, the buffer solutions containing weak base and its salt are called **basic buffer solutions** e.g. a buffer containing a mixture of ammonium hydroxide and ammonium chloride;  $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ . Let us learn about the way a buffer solution perform its function.

### 8.6.1 Buffer Action

In order to understand the action of a buffer solution we take the example of a common acidic buffer viz., acetic acid –sodium acetate buffer. As stated above it consist of a mixture of acetic acid and sodium acetate. The ionisation of acetic acid and dissociation of sodium acetate can be given as



You may recall from example 8.5 that in a mixture of acetic acid and sodium acetate the degree of ionisation of acetic acid decreased from an initial low value. This means that at equilibrium very few of the acetic acid molecules are ionised. In other words, for all practical purposes the concentration of acetic acid molecules in the solution is equal to the concentration of acetic acid taken initially. Similarly, sodium acetate being a salt gets fully dissociated and provides an equivalent amount of acetate ions. In addition to these, a negligibly small number of acetate ions are obtained from ionisation of acetic acid. In other words, for all practical purposes the concentration of acetate ions in the solution is equal to the concentration of sodium acetate taken initially. On the other hand, the concentration of hydronium ions is much smaller as compared to the concentrations of acetic acid and sodium acetate. Thus, you can see that a buffer system contains a conjugate acid-base pair (acetic acid -acetate ion here) and the concentrations of these two are quite high as compared to that of the hydronium ions. The conjugate acid and base constituting the buffer are called **acid reserve** and the **base reserve** respectively. These provide ‘buffering’ against the added base and acid respectively. Let’s see their mode of action.

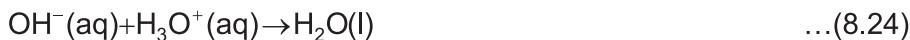
If we add a small amount of a strong acid such as HCl to a buffer solution containing acetic acid and sodium acetate, the added  $\text{H}_3\text{O}^+$  ions would react with an equivalent amount of the base reserve in the buffer i.e.,  $\text{CH}_3\text{COO}^-$  ions to generate undissociated acetic acid. The reaction can be given as



A buffer system contains a conjugate acid- base pair and the concentrations of these two are quite high as compared to that of the hydronium ions.

Some of the acetic acid molecules so obtained would dissociate back, but the number would be too small to be significant. The net effect would be that the concentration of acetic acid would increase slightly whereas that of acetate ions (base reserve) would decrease slightly. The concentration of hydronium ions and thus the pH of the solution would not change significantly as the added hydronium ions are consumed by reaction with acetate ions.

Similarly, when small amounts of a strong base like NaOH is added, the hydroxyl ions produced by it would react with an equivalent amount of hydronium ions and neutralise them to produce water as per the following reaction

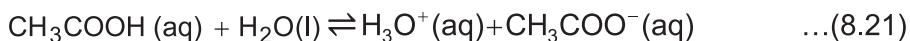


Some of the hydronium ions present in the solution get consumed in the process. In order to compensate for that some of the acetic acid molecules (acid reserve) ionise to provide hydronium ions and maintain the equilibrium. However, these would generate some additional acetate ions roughly equal to the amount of added hydronium ions. The net effect would be that the concentration of acetic acid would decrease slightly whereas that of acetate ions would increase slightly; but the concentration of hydronium ions and thus the pH of the solution would not change significantly.

You may note here that the added acid or the base only cause minor changes in the concentrations of the weak acid and the salt constituting the buffer solution. On the other hand, the concentration of the hydronium ions and thus the pH does not change significantly. Let us derive a mathematical expression for determining the pH of a buffer solution.

### 8.6.2 Henderson-Hasselbalch Equation

The Henderson-Hasselbalch equation relates the pH of a given buffer solution to the concentrations of its components viz. weak acid / base and the salt containing common ion. In order to derive this expression we again take the example of acetic acid-sodium acetate buffer. As given above, the acetic acid ionises in water and the following equilibrium is established



The equilibrium is characterised by the following acid ionisation constant

$$K_a = \frac{[\text{H}_3\text{O}^+] [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad \dots(8.25)$$

The ionisation constant expression can be rearranged to give,

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \quad \dots(8.26)$$

As discussed above, for all practical purposes, the concentration of undissociated acetic acid in the buffer solution can be taken as initial acid concentration [Acid], and the concentration of acetate ions equals the total sodium acetate concentration, i.e., [Salt]. In the light of this the Eq. (8.26) may be rewritten as

$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{Acid}]}{[\text{Salt}]} \quad \dots(8.27)$$

You may note here that  $K_a$  is a constant so the concentration of hydronium ions depends directly on the ratio of acid to salt concentrations; higher the ratio more the hydronium ion concentration.

Taking log on the both sides of Eq. (8.27) we get,

$$\log [\text{H}_3\text{O}^+] = \log K_a + \log \frac{[\text{Acid}]}{[\text{Salt}]} \quad \dots(8.28)$$

multiplying throughout by  $(-1)$  gives

$$-\log [\text{H}_3\text{O}^+] = -\log K_a - \log \frac{[\text{Acid}]}{[\text{Salt}]} \quad \dots(8.29)$$

$$\Rightarrow \text{pH} = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad \because \text{pH} = -\log [\text{H}_3\text{O}^+]; \quad pK_a = -\log K_a \quad \dots(8.30)$$

This is known as **Henderson-Hasselbalch equation** for an acidic buffer. We can derive a similar expression for a basic buffer (e.g., ammonium hydroxide and ammonium chloride). The expression for a basic buffer would be

$$\Rightarrow \text{pOH} = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \quad \dots(8.31)$$

These equations are very handy in calculating the pH values of common buffer solutions. Let's take up some simple examples to see the application of these equations.

**Example 8.6:** Calculate the pH of a buffer solution containing 0.1 M acetic acid and 0.5 M sodium acetate.

[Given:  $K_a$  (acetic acid) =  $1.8 \times 10^{-5}$ ]

**Solution:** As per the Henderson-Hasselbalch equation the pH of an acidic buffer solution is given by the following expression

$$\text{pH} = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad \dots(8.30)$$

First let's compute the value of  $pK_a$

$$pK_a = -\log K_a = -\log [1.8 \times 10^{-5}] = -[-4.74] = 4.74$$

Given: [acetic acid] = 0.1 M and [sodium acetate] = 0.5 M

Substituting in the Eq. (8.30) we get

$$\text{pH} = 4.74 + \log \frac{[0.5]}{[0.1]} = 4.74 + \log 5 = 4.74 + 0.6990 = 5.44$$

Thus, the pH of the given buffer solution would be 5.44

**Example 8.7:** Calculate the pH of a buffer solution containing 0.1 M ammonium hydroxide and 0.2 M ammonium chloride at 298 K.  
 [Given:  $K_b$  (ammonium hydroxide) =  $1.8 \times 10^{-5}$ ]

**Solution:** As per the Henderson-Hasselbalch equation the pOH of a basic buffer solution is given by the following expression

$$\Rightarrow \text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \quad \dots(8.31)$$

First let's compute the value of  $\text{p}K_b$

$$\text{p}K_b = -\log K_b = -\log[1.8 \times 10^{-5}] = -[-4.74] = 4.74$$

Given: [ammonium hydroxide] = 0.1 M and [ammonium chloride] = 0.2 M

Substituting the values in the Eq. (8.31), we get

$$\text{pOH} = 4.74 + \log \frac{[0.2]}{[0.1]} = 4.74 + \log 2 = 4.74 + 0.3010 = 5.04$$

You know that at 298 K,  $\text{pH} + \text{pOH} = 14$

$$\Rightarrow \text{pH} = 14.0 - 5.04 = 8.96$$

Thus, the pH of the given buffer solution would be 8.96

**Example 8.8:** Calculate the pH of a buffer solution prepared by mixing 40 cm<sup>3</sup> of 0.1 M acetic acid and 60 cm<sup>3</sup> of 0.5 M sodium acetate.  
 [Given:  $K_a$  (acetic acid) =  $1.8 \times 10^{-5}$ ]

**Solution:** As in example 8.6 the pH can be obtained by using Henderson-Hasselbalch equation, viz.,

$$\Rightarrow \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad \dots(8.30)$$

We have already calculated the  $\text{p}K_a$  value for acetic acid to be 4.74.

Now we need to calculate the concentrations of acetic acid and sodium acetate in the buffer solution. We are given that 40 cm<sup>3</sup> of acetic acid and 60 cm<sup>3</sup> of sodium acetate are mixed, which makes the total volume of the solution to be 100 cm<sup>3</sup>. The concentrations of acetic acid and sodium acetate in the buffer can be obtained by using dilution equation viz.,  $M_1V_1 = M_2V_2$

$$\text{Concentration of acetic acid in the buffer} = M_2 = \frac{M_1V_1}{V_2} = \frac{0.1 \times 40}{100} = 0.04 \text{ M}$$

$$\text{Concentration of sodium acetate in the buffer} = M_2 = \frac{M_1V_1}{V_2} = \frac{0.5 \times 60}{100} = 0.30 \text{ M}$$

Substituting the values in the Henderson-Hasselbalch equation we get,

$$\Rightarrow \text{pH} = 4.74 + \log \frac{[0.30]}{[0.04]} = 4.74 + \log 7.5 = 4.74 + 0.875 = 5.62$$

Thus, the pH of the given buffer solution would be 5.62

### 8.6.3 Buffer Capacity

It is important to know that all the buffer solutions of a given buffer system are not equally effective. The effectiveness of a given buffer is expressed in terms of a term called **buffer capacity** and refers to its ability to resist pH change on adding small volumes of an acid or a base solution. It can also be visualised as the tolerance of the buffer towards the addition of acid/base solution. The buffer capacity of a given buffer depends on the absolute concentrations of the acid and base reserves as well as their relative amounts.

A buffer containing higher concentration of weak acid/base and the salt has a higher capacity to resist change in pH value. This means adding a certain amount of strong acid or base to a buffer containing higher concentration of buffer components would show lesser change in pH as compared to a buffer containing lower concentrations of the constituents. A buffer containing 0.5 M each of acetic acid and sodium acetate has a higher buffer capacity than that containing 0.1M each of the components. You may note that to begin with, both the buffers would have same pH value.

You would recall from the buffer action discussed in Section 8. 2 that addition of small amounts of strong acid / base to a buffer slightly alters the amounts of the components of the buffer. Also, the pH of the buffer depends on the ratio of the buffer components; Eq. (8.30) and Eq. (8.31). For a buffer having similar concentrations of acid / base and its salt the change in their ratio on adding small volumes of strong acid / base is much less than that for a buffer having different concentrations of acid / base and its salt. Therefore, a buffer containing similar concentration of its components has a higher buffer capacity than the buffers containing different concentrations of the buffer components. In conclusion we can say that the buffers containing higher absolute concentrations of its components and the ones containing similar concentrations of its components have a better ability to resist the change in pH on addition of small volumes of strong acid/base solutions.

According to IUPAC, buffer capacity is defined as, “The capacity of a solution to resist changes in pH on the addition of strong acid or strong base which may be expressed numerically as the number of moles of strong acid or strong base required to change the pH by one unit when added to one litre of the specified buffer solution”.

#### SAQ 6

Calculate the pH of a buffer solution prepared by mixing 100 cm<sup>3</sup> of 0.3 M acetic acid with 200 cm<sup>3</sup> of 0.6 M solution of sodium acetate.[ Given:  $K_a$  (acetic acid=  $1.8 \times 10^{-5}$ )]

#### SAQ 7

Which of the following buffer solutions would have the highest buffer capacity?

- a) Buffer containing 1.0 M acetic acid and 0.1 M sodium acetate
- b) Buffer containing 1.0 M acetic acid and 1.0 M sodium acetate
- c) Buffer containing 0.1 M acetic acid and 0.1 M sodium acetate
- d) Buffer containing 0.5 M acetic acid and 1.0 M sodium acetate

Justify your answer.

## 8.7 SUMMARY

In this unit we continued our discussion on ionic equilibrium and started by taking up the ionisation equilibria associated with the ionisation of weak acids and weak bases. In this context we talked about degree of ionisation of weak acids and bases and the way to express the ionisation constants characterising the respective ionisation equilibria. As the magnitude of ionisation equilibrium constant or just ionisation constant is proportional to the degree of ionisation, it conveys about the strength of the acid / base; higher the magnitude of ionisation constant, stronger the acid / base. We also explained the logic and procedure to calculate the pH of a solution of a weak acid or base using the value of ionisation constant or calculating ionisation constant using the pH of the solution.

The discussion on the ionisation of weak acids and bases was followed by a discussion on the ionisation equilibria and the corresponding ionisation constants for diprotic and polyprotic acids. In this process you learnt that diprotic and polyprotic acids undergo sequential ionisation wherein each time one of the ionisable protons gets ionised. The ionisation constant of the first stage of ionisation has a relatively higher magnitude and the successive ionisation constants get smaller and smaller. We also explained the procedure to calculate the concentration of all the species present in an aqueous solution of a triprotic acid.

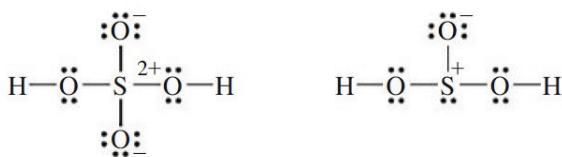
The addition of a salt containing an ion common with the weak acid or a weak base suppresses its ionisation and thus decreases its degree of ionisation. You have learnt that by changing the amount of salt containing a common ion added to a solution of a weak acid/base we can control the extent of ionisation of the weak acid/base and thus can control its pH. This fact is used in buffer solutions, which may be defined as the solutions that resist the change in their pH on addition of small volumes of solutions of strong acids or strong bases or on dilution. A buffer solution typically contains a weak acid or a weak base and a salt having an ion common with the acid/base. We explained the way buffers perform their function and also derived expressions to compute the pH value of a buffer solution and used the same to calculate the pH of some buffer solutions.

Towards the end, we discussed about buffer capacity—the ability of a buffer to resist change in pH. We stated that buffer solutions containing higher absolute concentrations of the acid/base and salt have higher buffer capacity and also that the buffers in which the concentration of the constituents is similar have better buffer capacity.

## 8.8 TERMINAL QUESTIONS

1. Define ionisation constant. What is the significance of ionisation constant of a weak base?
2. Formic acid ( $\text{HCOOH}$ ) is a weak acid. Write the ionisation equilibrium reaction for formic acid in water and also give expression for the corresponding ionisation constant.

3. How would the degree of ionisation of a weak acid change with dilution of its solution? Explain
4. Dimethylamine,  $(\text{CH}_3)_2\text{NH}$ , is a weak base having  $K_b = 5.1 \times 10^{-4}$ . Calculate the pH of a 0.2 M aqueous solution of dimethylamine at 298 K.
5. The pH of an aqueous solution of lactic acid,  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ -a weak acid, was found to be 2.7. Calculate the concentration of the solution if  $K_a$  (lactic acid) =  $1.4 \times 10^{-4}$ .
6. The Lewis structures of sulphuric and sulphurous acids are given below. Predict which one of these would be a stronger acid on the basis of given structures.



7. Adipic acid,  $\text{HOOC}(\text{CH}_2)_4\text{COOH}$  is a diprotic acid with the acid dissociation constants as  $K_{a1} = 3.9 \times 10^{-5}$  and  $K_{a2} = 3.9 \times 10^{-6}$ . Calculate the concentrations of all the ionic species present in 0.1 M aqueous solution of adipic acid.
8. Explain the effect of common ions on the ionisation equilibrium of weak acids with the help of a suitable example.
9. Define buffer solutions. Write the expression for the pH of a basic buffer solution.
10. Calculate the pH values for the following buffer solutions containing:
  - i) 1.5 M acetic acid and 1.5 M sodium acetate
  - ii) 0.15 M acetic acid and 0.15 M sodium acetate

Which of these buffer solutions would have a higher buffer capacity?

## 8.9 ANSWERS

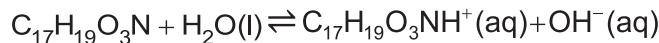
### Self-Assessment Questions

1. The degree of ionisation ( $\alpha$ ) and the ionisation constant ( $K_a$ ) for a weak acid are related as:

$$K_a = \frac{c\alpha^2}{(1-\alpha)}$$

According to the relation given above, a higher ionisation constant implies a higher degree of ionisation. Thus, the magnitude of ionisation constant of a weak acid is a measure of the strength of the acid; higher the value stronger the acid.

2. The ionisation of morphine can be represented as



If we assume that the degree of ionisation of the solution at given concentration is  $\alpha$ , the initial and equilibrium concentrations of different species in the solution would be as follows:

Concentration/ mol dm <sup>-3</sup>	$\text{C}_{17}\text{H}_{19}\text{O}_3\text{N(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{C}_{17}\text{H}_{19}\text{O}_3\text{NH}^+(\text{aq}) + \text{OH}^-(\text{aq})$		
Initial	0.01	0	0
Change due to ionisation	$-0.01\alpha$	$0.01\alpha$	$0.01\alpha$
At equilibrium	$0.01(1 - \alpha)$	$0.01\alpha$	$0.01\alpha$

We can write the expression for  $K_b$  as,  $K_b = \frac{c\alpha^2}{(1-\alpha)}$

$$K_b = \frac{0.01\alpha^2}{(1-\alpha)}$$

Assuming that for weak base the degree of ionisation,  $\alpha$ , is small as compared to 1, we can ignore it in the denominator, we get  $K_b = 0.01\alpha^2$

$$\text{Which gives, } \alpha = \sqrt{\frac{K_b}{0.01}}$$

Substituting the value of the equilibrium constant,

$$\alpha = \sqrt{\frac{1.6 \times 10^{-6}}{0.01}} = \sqrt{1.6 \times 10^{-4}} = 0.0126$$

Degree of ionisation = 0.0126  $\rightarrow$  Percentage ionisation = 1.26%

As the value of degree of ionisation is less than 5%, our assumption is justified.

From the table above, we see that the concentration of hydroxide ions,  $[\text{OH}^-]$  at equilibrium =  $0.01 \times \alpha$

$$\rightarrow [\text{OH}^-] = 0.01 \times 0.0126 = 0.000126 = 1.26 \times 10^{-4} \text{ M}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log[1.26 \times 10^{-4}]$$

$$\text{pOH} = -(-3.90) = 3.90$$

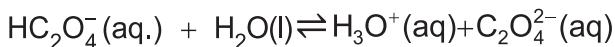
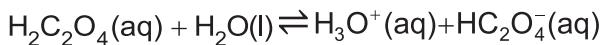
we know that at 298 K,  $\text{pH} + \text{pOH} = 14$

$$\text{pH} = 14 - \text{pOH}$$

$$\rightarrow \text{pH} = 14 - 3.90 = 10.10$$

Thus, the pH of 0.01 M solution of morphine would be 10.10.

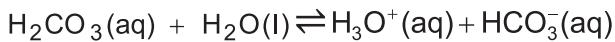
3. The equilibrium reactions for the successive ionisation of oxalic acid are as under:



The corresponding equilibrium constant expressions are:

$$K_{a1} = \frac{[\text{HC}_2\text{O}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{C}_2\text{O}_4]} \quad \text{and} \quad K_{a2} = \frac{[\text{C}_2\text{O}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{HC}_2\text{O}_4]}$$

4. The equilibrium reaction for the first stage of ionisation of carbonic acid can be given as;



If  $\alpha$  is the degree of ionisation of the carbonic acid at the given concentration, the initial and equilibrium concentrations of different species in the solution would be as follows

Concentration/ mol dm <sup>-3</sup>	$\text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})$		
Initial	1.0	0	0
Change due to ionisation	$-\alpha$	$\alpha$	$\alpha$
At equilibrium	$1 - \alpha$	$\alpha$	$\alpha$

The equilibrium constant for the ionisation reaction is given as

$$K_{a1} = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{CO}_3]}$$

Substituting the value of the ionisation constant and the equilibrium concentrations from the table above in the equilibrium constant expression, we get

$$4.4 \times 10^{-7} = \frac{\alpha \alpha}{1 - \alpha} \Rightarrow \frac{\alpha^2}{1 - \alpha}$$

Since it is assumed to be a weak acid, ignoring  $\alpha$  in the denominator we get,

$$\alpha^2 = 4.4 \times 10^{-7} \Rightarrow \alpha = 0.00066$$

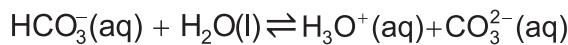
As the value of  $\alpha$  is about 0.07% so our assumption is valid and we get the concentrations of bicarbonate and hydronium ions as

$$[\text{HCO}_3^-] = [\text{H}_3\text{O}^+] = c\alpha$$

Substituting the values

$$\Rightarrow [\text{HCO}_3^-] = [\text{H}_3\text{O}^+] = 1 \times 6.6 \times 10^{-4} = 6.6 \times 10^{-4} \text{ M}$$

The equilibrium equation for the second stage of ionisation of carbonic acid can be given as;



Assuming  $\alpha$  to be the degree of ionisation, the initial and equilibrium concentrations of different species in the solution would be as follows

Concentration/ mol dm <sup>-3</sup>	$\text{HCO}_3^- (\text{aq}) + \text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$		
Initial	$6.6 \times 10^{-4}$	$6.6 \times 10^{-4}$	0
Change due to ionisation	$-6.6 \times 10^{-4} \alpha$	$6.6 \times 10^{-4} \alpha$	$6.6 \times 10^{-4} \alpha$
At equilibrium	$6.6 \times 10^{-4} (1 - \alpha)$	$6.6 \times 10^{-4} (1 + \alpha)$	$6.6 \times 10^{-4} \alpha$

The equilibrium constant expression for second stage of ionisation

$$K_{a2} = \frac{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]}$$

Substituting the equilibrium concentrations from the table in the equilibrium constant expression, we get

$$\frac{[6.6 \times 10^{-4} (1 + \alpha)][6.6 \times 10^{-4} \alpha]}{[6.6 \times 10^{-4} (1 - \alpha)]} = 4.7 \times 10^{-11}$$

Since the second stage ionisation is like that of a weak acid, we can assume  $\alpha$  to be negligible as compared to 1 in the numerator and denominator, we get

$$[6.6 \times 10^{-4} \alpha] = 4.7 \times 10^{-11}$$

$$\alpha = \frac{4.7 \times 10^{-11}}{6.6 \times 10^{-4}} = 7.1 \times 10^{-8}$$

$$\Rightarrow \alpha = 7.1 \times 10^{-8}$$

As the value of  $\alpha$  is quite small as compared to the initial concentration of bicarbonate ions ( $6.6 \times 10^{-4}$  M) our ignoring it is justified.

From the table above, the concentration of  $\text{CO}_3^{2-}$  ions =  $6.6 \times 10^{-4} \alpha$

$$\Rightarrow [\text{CO}_3^{2-}] = 6.6 \times 10^{-4} \times 7.1 \times 10^{-8} = 4.7 \times 10^{-11} \text{ M}$$

So the concentration of  $\text{CO}_3^{2-}$  ions would be =  $4.7 \times 10^{-11}$  M

The concentration of  $\text{H}_2\text{CO}_3$  would be equal to the initial concentration (1.0 M) minus the degree of ionisation of first stage i.e.,

$$1.0 - 0.00066 = 0.99934 \text{ M}$$

So the concentrations of different species in the 1.0 M solution of carbonic acid would be

$$[\text{HCO}_3^-] = 6.6 \times 10^{-4} \text{ M} \quad [\text{H}_3\text{O}^+] = 6.6 \times 10^{-4} \text{ M}$$

$$[\text{CO}_3^{2-}] = 4.7 \times 10^{-11} \text{ M} \quad [\text{H}_2\text{CO}_3] = 0.99934 \text{ M}$$

5. In case of nitric acid there are two oxygen atoms attached to the nitrogen atom, whereas nitrous acid has only one. Due to higher electronegativity, these would withdraw electrons from nitrogen atom and make the OH bond polar leading to greater tendency to lose proton. As there are two such oxygen atoms in nitric acid, the effect would be more pronounced in it and nitric acid would be stronger than nitrous acid.
6. According to the Henderson-Hasselbalch equation the pH of the acetic acid-sodium acetate buffer would be given as

$$\Rightarrow \text{pH} = \text{p}K_a + \log \frac{[\text{Sodium acetate}]}{[\text{Acetic acid}]}$$

First let's compute the value of  $\text{p}K_a$

$$\text{p}K_a = -\log K_a = -\log [1.8 \times 10^{-5}] = -[-4.74] = 4.74$$

The concentrations of sodium acetate and acetic acid in the buffer mixture can be calculated by using dilution formula.

The total volume of the solution =  $100 \text{ cm}^3 + 200 \text{ cm}^3 = 300 \text{ cm}^3$ .

Concentration of acetic acid in the buffer solution

$$M_2 = \frac{M_1 V_1}{V_2} = \frac{0.3 \times 100}{300} = 0.10 \text{ M}$$

Concentration of sodium acetate in the buffer solution

$$M_2 = \frac{M_1 V_1}{V_2} = \frac{0.6 \times 200}{300} = 0.40 \text{ M}$$

The pH can be calculated using Henderson-Hasselbalch equation, viz.,

$$\Rightarrow \text{pH} = \text{p}K_a + \log \frac{[\text{Sodium acetate}]}{[\text{Acetic acid}]}$$

Substituting the values in the equation we get,

$$\Rightarrow \text{pH} = 4.74 + \log \frac{[0.40]}{[0.10]} = 4.74 + \log 4$$

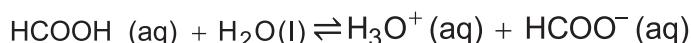
$$= 4.74 + 0.602 = 5.34$$

Thus the pH of the given buffer solution would be **5.34**

7. b) As this buffer has the maximum absolute concentrations of the components of the buffer and also the two concentrations are equal.

## **Terminal Questions**

1. The ionisation constant refers to the equilibrium constant for the ionisation reaction of a weak acid or a weak base. The ionisation constant for a weak base is a measure of the extent of its ionisation. Higher the value of the ionisation constant greater the ionisation and thus stronger the base
2. The equilibrium reaction for the ionisation of formic acid, can be given as under:



The ionisation constant expression for ionisation of formic acid would be

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

3. The degree of ionisation of a weak acid increases with dilution. In order to understand the variation of degree of ionisation with dilution we write the expression relating the ionisation constant and degree of ionisation for a weak acid as

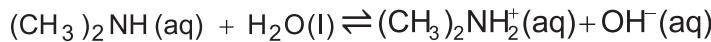
$$K_a = c\alpha^2$$

As the concentration varies inversely with volume of the solution containing unit amount of the solute, we write,  $c=1/V$ . Substituting in the above equation we get,

$$K_a = \frac{1}{V}\alpha^2$$

If dilution increases, the value of  $1/V$  decreases and to keep  $K_a$  constant, the degree of ionisation increases. Thus the degree of ionisation increases with dilution.

4. The equilibrium reaction for the ionisation of dimethylamine in water, can be given as under:



If the degree of ionisation of dimethylamine in this solution is  $\alpha$ , the initial and equilibrium concentrations of various species in the solution would be

Concentration/ mol dm <sup>-3</sup>	$(\text{CH}_3)_2\text{NH} \text{ (aq)} + \text{H}_2\text{O(l)} \rightleftharpoons (\text{CH}_3)_2\text{NH}_2^+ \text{ (aq)} + \text{OH}^- \text{ (aq)}$		
Initial	0.1	0	0
Change due to ionisation	$-0.1\alpha$	$0.1\alpha$	$0.1\alpha$
At equilibrium	$0.1(1-\alpha)$	$0.1\alpha$	$0.1\alpha$

We can write the following expression relating the base ionisation constant and degree of ionisation.

$$K_b = \frac{c\alpha^2}{(1-\alpha)} \Rightarrow K_b = \frac{0.1\alpha^2}{(1-\alpha)}$$

Assuming that for the weak base  $\alpha$ , is small as compared to 1, we can ignore it in the denominator, we get

$$K_b = 0.1\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_b}{0.1}}$$

Substituting the values of  $K_b$ ,

$$\alpha = \sqrt{\frac{5.1 \times 10^{-4}}{0.1}} = \sqrt{5.1 \times 10^{-3}} = 0.072$$

Degree of ionisation,  $\alpha = 0.072$

The value of degree of ionisation (0.072) is more than 5% of the initial concentration, so our assumption of it being small and neglecting it is not valid. So going back to the expression for  $K_b$ , we had

$$\Rightarrow K_b = \frac{0.1\alpha^2}{(1-\alpha)}$$

Substituting the value of ionisation constant again,

$$\Rightarrow 5.1 \times 10^{-4} = \frac{0.1\alpha^2}{(1-\alpha)}$$

Simplifying and rearranging, we get

$$\begin{aligned} (5.1 \times 10^{-4}) - (5.1 \times 10^{-4})\alpha &= 0.1\alpha^2 \\ \Rightarrow 0.1\alpha^2 + (5.1 \times 10^{-4})\alpha - (5.1 \times 10^{-4}) &= 0 \end{aligned}$$

We need to solve the above quadratic equation to get the degree of dissociation. You may recall that for a quadratic equation,  $ax^2 + bx + c = 0$ , the value of  $x$  can be obtained by the following equation

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In case of our quadratic equation, we get

$$\Rightarrow \alpha = \frac{-(5.1 \times 10^{-4}) \pm \sqrt{(5.1 \times 10^{-4})^2 - 4 \times 0.1 \times (-5.1 \times 10^{-4})}}{2 \times 0.1}$$

$$\Rightarrow \alpha = \frac{-(5.1 \times 10^{-4}) \pm \sqrt{(2.60 \times 10^{-7}) + (2.04 \times 10^{-4})}}{0.2}$$

$$\Rightarrow \alpha = \frac{-(5.1 \times 10^{-4}) \pm \sqrt{2.04 \times 10^{-4}}}{0.2}$$

$$\Rightarrow \alpha = \frac{-(5.1 \times 10^{-4}) \pm 1.43 \times 10^{-2}}{0.2} = \frac{1.38 \times 10^{-2}}{0.2} = 6.9 \times 10^{-2}$$

$$\alpha = 6.9 \times 10^{-2}$$

From the table above, we see that the concentration of hydroxide ions,  $[\text{OH}^-]$  at equilibrium =  $0.1 \times \alpha = 0.1 \times 0.069 = 0.0069 = 6.9 \times 10^{-3} \text{ M}$

We know that

$$\text{pOH} = -\log[\text{OH}^-]$$

Substituting the value of  $[\text{OH}^-]$

$$\text{pOH} = -\log [6.9 \times 10^{-3}]$$

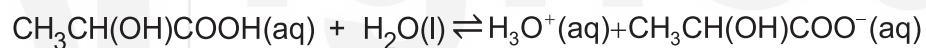
$$\text{pOH} = -(-2.16) = 2.16$$

You know that at 298 K,  $\text{pH} + \text{pOH} = 14$

$$\text{pH} = 14 - \text{pOH}$$

$$\Rightarrow \text{pH} = 14 - 2.16 = 11.84$$

5. The equilibrium reaction for the ionisation of the weak acid-lactic acid,  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ , can be given as under:



If the degree of ionisation of  $c \text{ mol dm}^{-3}$  solution of lactic acid is assumed to be  $\alpha$ , the initial and equilibrium concentrations of various species in the solution would be

Concentration / $\text{mol dm}^{-3}$	$\text{CH}_3\text{CH}(\text{OH})\text{COOH(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{CH}(\text{OH})\text{COO}^-(\text{aq})$
Initial	$c$ 0      0
Change due to ionisation	$-c\alpha$ $c\alpha$ $c\alpha$
At equilibrium	$c(1-\alpha)$ $c\alpha$ $c\alpha$

The equilibrium constant for the ionisation reaction of lactic acid can be written as

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CH}(\text{OH})\text{COO}^-]}{[\text{CH}_3\text{CH}(\text{OH})\text{COOH}]}$$

Substituting the concentrations of different species at equilibrium in the expression we get,

$$K_a = \frac{c\alpha \times c\alpha}{c(1-\alpha)} \Rightarrow cK_a = \frac{c^2\alpha^2}{(1-\alpha)}$$

As lactic acid is a weak acid, we can ignore  $\alpha$  in the denominator, we get

$$cK_a = c^2\alpha^2$$

From the table above we see that  $c\alpha$  is equal to the concentration of hydronium ions. Substituting,

$$cK_a = [\text{H}_3\text{O}^+]^2$$

$$c = \sqrt{\frac{[\text{H}_3\text{O}^+]^2}{K_a}}$$

So we can calculate the concentration of hydronium ions from the given value of pH and substitute the same in the above expression to get the concentration of the solution.

Let's now calculate the concentration of hydronium ions:

We know that  $\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] \rightarrow [\text{H}_3\text{O}^+] = \text{antilog}(-\text{pH})$

$$\rightarrow [\text{H}_3\text{O}^+] = \text{antilog}(-3.7) = 2.0 \times 10^{-4} \text{ M}$$

We know that,

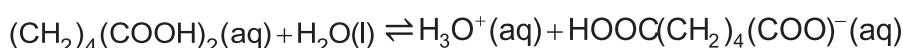
$$c = \sqrt{\frac{[\text{H}_3\text{O}^+]^2}{K_a}}$$

Substituting the values of hydronium ion concentration and of  $K_a$ , we get

$$\Rightarrow c = \sqrt{\frac{(2 \times 10^{-4})^2}{1.4 \times 10^{-7}}} = \sqrt{\frac{4 \times 10^{-8}}{1.4 \times 10^{-7}}} = \sqrt{0.286} = 0.5345 \text{ M}$$

Thus, the concentration of the given solution of lactic acid is found to be 0.5345 M

6. In case of sulphuric acid, there are two oxygen atoms attached to the sulphur besides the hydroxyl group whereas there is only one such oxygen atom in sulphurous acid. These oxygen atoms would withdraw electrons from sulphur atom due to their higher electronegativity. This in turn would make the OH bond more polar leading to its greater tendency to lose proton. Due to two such oxygen atoms the hydroxyl groups would be more polar in sulphuric acid than that in sulphurous acid. Therefore, of the given two acids, sulphuric acid would be stronger.
7. The equilibrium reaction for the first stage of ionisation of adipic acid can be given as;



If  $\alpha$  is the degree of ionisation of adipic acid in the given solution, the initial and equilibrium concentrations of different species in 0.1 M solution of adipic acid would be as follows

Concentration/ mol dm <sup>-3</sup>	$(\text{CH}_2)_4(\text{COOH})_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HOOC}(\text{CH}_2)_4(\text{COO}^-)(\text{aq})$		
Initial	0.1	0	0
Change due to ionisation	$-0.1\alpha$	$0.1\alpha$	$0.1\alpha$
At equilibrium	$0.1(1-\alpha)$	$0.1\alpha$	$0.1\alpha$

The equilibrium constant for the reaction would be

$$K_{a1} = \frac{[\text{HOOC}(\text{CH}_2)_4\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{HOOC}(\text{CH}_2)_4\text{COOH}]}$$

Substituting the equilibrium concentrations from the table in the equilibrium constant expression, we get

$$K_{a1} = \frac{[0.1\alpha][0.1\alpha]}{0.1[1-\alpha]} = \frac{[0.1\alpha^2]}{[1-\alpha]}$$

Substituting the value of  $K_a$ ,

$$3.9 \times 10^{-5} = \frac{[0.1\alpha^2]}{[1-\alpha]}$$

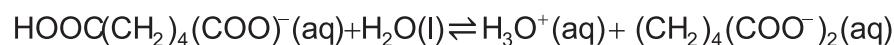
As adipic acid is a weak acid, therefore, ignoring  $\alpha$  in the denominator we get,

$$0.1\alpha^2 = 3.9 \times 10^{-5} \Rightarrow \alpha = 0.00197$$

As the value of  $\alpha$  is about 0.2% our assumption is valid. From the table we can write,

$$\rightarrow [\text{HOOC}(\text{CH}_2)_4\text{COO}^-] = [\text{H}_3\text{O}^+] = c\alpha = 0.1 \times 0.00197 = 1.97 \times 10^{-4}$$

Now, the equation for the second stage of ionisation of adipic acid can be given as;



Again, assuming  $\alpha$  to be the degree of ionisation, the initial and equilibrium concentrations of different species would be as follows

Concentration/ mol dm <sup>-3</sup>	$\text{HOOC}(\text{CH}_2)_4(\text{COO}^-)(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + (\text{CH}_2)_4(\text{COO}^-)_2(\text{aq})$		
Initial	$1.97 \times 10^{-4}$	$1.97 \times 10^{-4}$	0
Change due to ionisation	$-1.97 \times 10^{-4}\alpha$	$1.97 \times 10^{-4}\alpha$	$1.97 \times 10^{-4}\alpha$
At equilibrium	$1.97 \times 10^{-4}(1-\alpha)$	$1.97 \times 10^{-4}(1+\alpha)$	$1.97 \times 10^{-4}\alpha$

The equilibrium constant expression for second stage of ionisation of adipic acid would be

$$K_{a2} = \frac{[(\text{CH}_2)_4(\text{COO}^-)_2][\text{H}_3\text{O}^+]}{[\text{HOOC}(\text{CH}_2)_4\text{COO}^-]}$$

Substituting the equilibrium concentrations from the table in the equilibrium constant expression, we get

$$\frac{[1.97 \times 10^{-4}(1+\alpha)][1.97 \times 10^{-4}\alpha]}{[1.97 \times 10^{-4}(1-\alpha)]} = 3.9 \times 10^{-6}$$

For the weak acid, assuming  $\alpha$  to be negligible as compared to 1 in the numerator and denominator, we get

$$[1.97 \times 10^{-4}\alpha] = 3.9 \times 10^{-6}$$

$$\alpha = \frac{3.9 \times 10^{-6}}{1.97 \times 10^{-4}} = 1.98 \times 10^{-2}$$

$$\Rightarrow \alpha = 1.98 \times 10^{-2}$$

From table, the concentration of  $(\text{CH}_2)_4(\text{COO}^-)_2$  ions would be

$$= 1.97 \times 10^{-4}\alpha \text{ M}$$

Substituting the value for  $\alpha$ ,

$$= 1.97 \times 10^{-4} \times 1.98 \times 10^{-2} \text{ M}$$

$$= 3.9 \times 10^{-6} \text{ M}$$

The concentration of undissociated adipic acid would be equal to the initial concentration (0.1 M) minus the concentration of hydronium ions i.e.,  $1.97 \times 10^{-4}$

$$0.10 - (1.97 \times 10^{-4}) = 0.0998$$

So the concentrations of different species in the 0.1 M solution of adipic acid would be

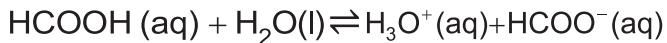
$$[\text{HOOC}(\text{CH}_2)_4\text{COO}^-] = [\text{H}_3\text{O}^+] = 1.97 \times 10^{-4} \text{ M}$$

$$[(\text{CH}_2)_4(\text{COO}^-)_2] = 3.90 \times 10^{-6} \text{ M}$$

$$[(\text{CH}_2)_4(\text{COOH})_2] = 9.98 \times 10^{-2} \text{ M}$$

8. The presence of common ions in an aqueous solution of a weak acid decreases the degree of ionisation of the weak acid. Let us understand with the help of the ionisation of formic acid (0.1 M) and the effect of addition of sodium formate (0.2 M) to it.  $K_a (\text{HCOOH}) = 1.7 \times 10^{-4}$ .

The equilibrium reaction for the ionisation of formic acid, can be given as under:



From example 8.1, the degree of ionisation of a weak acid is given as

$$\alpha = \sqrt{\frac{K_a}{c}}$$

$$\text{Substituting the values of } K_a \text{ and } c \text{ we get, } \alpha = \sqrt{\frac{1.7 \times 10^{-4}}{0.1}} = 0.0041$$

Thus, the degree of ionisation of formic acid in 0.1 M solution = 0.0041

We generally add solid salt so that there is no dilution

Now if we add sodium formate to the solution such that its concentration in solution is 0.2 M.

The salt sodium formate would dissociates as



If the degree of ionisation of formic acid in this solution of formic acid and sodium formate is  $\alpha$ , then the initial and equilibrium concentrations of various species in the solution would be

Concentration/mol dm <sup>-3</sup>	$\text{HCOOH (aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HCOO}^-(\text{aq})$		
Initial	0.1	0	0
Change due to ionisation of formic acid	$-0.1\alpha$	$0.1\alpha$	$0.1\alpha$
Change due to dissociation of sodium formate	0	0	0.2
At equilibrium	$0.1(1-\alpha)$	$0.1\alpha$	$0.2(1+0.5\alpha)$

We can write the expression for acid ionisation constant of formic acid as

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

Substituting the equilibrium concentrations of different species from the table, we get

$$K_a = \frac{[0.1\alpha][0.2(1+0.5\alpha)]}{[0.1(1-\alpha)]}$$

As formic acid is a weak acid and its degree of ionisation is further suppressed by the presence of formate ions (the common ion) we can reasonably assume that

$$\alpha \ll 1; \text{ and } (1-\alpha) \sim 1; \text{ also } (1 + 0.5\alpha) \sim 1$$

Under these conditions we can write

$$K_a = \frac{[0.1\alpha][0.2]}{[0.1]} = [0.2\alpha]$$

Substituting the value of the acid ionisation constant,  $K_a$

$$1.7 \times 10^{-4} = [0.2\alpha] \Rightarrow \alpha = 8.5 \times 10^{-4}$$

So the degree of ionisation of formic acid in the given solution = 0.00085.

→ The degree of ionisation of formic acid decreased from 0.0041 to 0.00085 due to the common ions provided by sodium formate.

9. A buffer solution can be defined as a solution that resists change in its pH on addition of small volumes of solutions of strong acids or bases or on slight dilution. A basic buffer solution consists of a weak base and a salt having an ion common with the weak base. The pH of a basic buffer solution is given by the following expression.

$$\Rightarrow pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Where [salt] refers to the concentration of the salt and [base] represents the concentration of weak base in the solution.  $pK_b$  is the negative log of the base ionisation constant  $K_b$ .

10. The pH of these solutions can be calculated by using Henderson-Hasselbalch equation,

$$\Rightarrow pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

First let's compute the value of  $pK_a$

$$pK_a = -\log K_a = -\log [1.8 \times 10^{-5}] = -[-4.74] = 4.74$$

- i) substituting the values we get

$$\Rightarrow pH = 4.74 + \log \frac{[1.5]}{[1.5]} = 4.74 + 0 = 4.74$$

$$\text{ii)} \Rightarrow pH = 4.74 + \log \frac{[0.15]}{[0.15]} = 4.74 + 0 = 4.74$$

Both of the buffer solutions would have same pH value of 4.74.

However, the buffer (i) having the higher concentrations of acid and the salt (1.5 M) would have a higher buffer capacity